

on the other hand, there is a weak focusing of the ions by the electric field of the potential barrier; the ion guide does not then have to extend right up to the field maximum. Since the saddle of the potential barrier is located behind the field maximum, and the saddle is usually in the center of an apertured diaphragm, this most important apertured diaphragm for generating the potential barrier can even be located at some distance outside the ion guide. The field barrier can also be located inside the ion guide, however, and can be shaped by potentials at the ion guide electrodes, e.g. at ring diaphragms of the ion guides, in such a way that a good mobility resolution is achieved.

**[0060]** The methods for measuring mobility spectra according to this invention do not use firm potential barriers but change the potential of the potential barrier (and with it the maximum of the axial field strength) continuously or incrementally. Consequently, in the first of these methods, more and more (or if the potential barrier is reduced, fewer and fewer) ion species are filtered out of a constant ion current from an ion source at the potential barrier due to the mobility of the ion species. An integral over the mobility spectrum of the ions is thus measured. A differentiation of the integral curves gives the mobility spectrum. This first spectrum acquisition method can be used by all embodiments of the invention including those not containing an ion guide.

**[0061]** With this first method, the ions of high mobility, which are held back, could create a space charge cloud which would disturb the further course of the method. This can be prevented by a suitable choice of RF and DC voltages at the electrodes of the ion guide (8) which ensures that most of these ions can escape laterally. These voltages at the ion guide can then advantageously be changed simultaneously with the height of the potential barrier, on the one hand to adapt the escape of ions of high mobility which are held back, and, on the other, to adapt the strength of the lateral guidance for the ions to the height of the opposing field.

**[0062]** A second spectrum acquisition method can be applied only by embodiments with ion guides between jet generating nozzle and field barrier. The ion guide is used as an ion storage device, which is filled by the ion beam from the ion source by keeping a high field barrier to prevent the ions escaping. After switching off the further supply of ions, the ions assemble in the axis of the storage device on the slope of the field barrier because they are pushed by the gas jet against the field barrier and collect at different heights according to their mobility. An axial electric field in the ion guide may support the drive of the ions against the field barrier. Ions with high mobility collect at the foot of the field barrier, where only a small electric field is present; those of low mobility, on the other hand, collect just below the field maximum. If the field barrier is now constantly lowered, one ion species after the other can be blown by the gas jet across the field maximum and escape in the direction of the ion detector. The mobility spectrum is thus measured directly, without the need for a differentiation. This second method is limited to about  $10^7$  ions, which can be stored in the ion guide without space charge effects having a noticeable disturbing effect. This limits the dynamic range of measurement, but to a remarkably large measurement range. By repeating the spectrum acquisition measurements several times, the dynamic range can be increased even further, however.

**[0063]** FIG. 1 is a schematic representation of an ion mobility spectrometer which can be used for both types of spectrum acquisition according to this invention because of the ion

guide (8) between the nozzle (6) and the field barrier generated by the apertured diaphragm (9). A conventional electrospray ion source (1, 2) outside the vacuum system supplies a mixture of ions together with curtain gas through inlet capillary (3) into a first vacuum chamber (4). Two ion funnels (5) and (8) in two vacuum chambers (4) and (7), and one ion detector (21) in vacuum chamber (10) are differentially evacuated by the vacuum pumps (22, 23, 24). The first ion funnel (5) guides the ions to the nozzle (6) which generates the gas jet (27) in chamber (7). Within the gas jet (27), the ions are kept in the axis by the second ion guide (8). Ion guide (8) is here shown to be an ion funnel with skimmers at the apertured diaphragms, but this ion guide also can be a special wing-type quadrupole ion guide as shown in FIG. 10. The potential barrier is preferably generated by a DC voltage at the ring diaphragm (9) at the end of the second ion funnel (8). The gas jet (27) blows the ions against the field barrier generated by the potential barrier. For the first spectrum acquisition method, the integral of the mobility spectrum is measured by increasing continuously the DC voltage for the potential barrier; and differentiating the ion current with respect to the potential barrier height to give the mobility spectrum. For the second spectrum acquisition method, the ion guide (8) is filled with ions, the further supply of ions from the ion source is stopped, and the mobility spectrum is directly measured by decreasing the field barrier.

**[0064]** Most of the embodiments described above including that of FIG. 1 can be coupled with mass spectrometers. An example is the arrangement according to FIG. 2, in which a time-of-flight mass spectrometer with orthogonal ion injection is coupled to the device used for measuring ion mobilities. The coupling here contains further ion guides (11, 13) and lens systems (12, 14), which form a thin ion beam (15). The time-of-flight mass spectrometer contains a pulser (17), which pulses out a section of the thin ion beam (15) perpendicular to the previous direction of flight of the ions and strongly accelerates it, and sends it as an ion beam (18) with high mass resolution to an ion detector (21) via an energy focusing reflector (20). There are several types of such time-of-flight mass spectrometers on the market; their operation is known to the specialist. Mass spectra can be acquired with high acquisition frequency of five to ten kilohertz. From series of mass spectra, acquired by changing the height of the potential barrier at the diaphragm (9), the ion current profiles for individual masses or mass ranges as a function of the height of the potential barrier can be extracted which, depending on the method, represent the mobility spectra of the ions either directly or as an integral. In FIG. 3, the integrals of the mobility spectra of individual mass ranges can be seen as they are obtained using the first method. Their differentiation then results in the ion-mass-specific mobility spectra shown in FIG. 4.

**[0065]** Using a commercial mass spectrometer with two ion funnels in the inlet region, as in FIG. 2, mobility resolutions of  $R_{mob}=40$  were obtained after only a short optimization, without changing the mechanical arrangement, and despite the relatively coarse potential steps selected. It can be expected that further optimizations will lead to higher resolutions. Further optimizations may concern the shape of the aperture (6), the pumping capacities of the differential pumping stages and hence the pressure difference at the aperture (6), the shape of the apertured diaphragms in the ion funnel (8) and, in particular, replacement of the single apertured